



Practitioner's Docket No. 50439-2

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of: Barstad et al.

Serial No.: 09/605,442

Group No.: 1741

Filed: June 28, 2004

Examiner: Wesley A. Nicolas

For: ELECTROLYTIC COPPER PLATING SOLUTION

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

AMENDMENT TRANSMITTAL

1. Transmitted herewith is an amendment for this application.

STATUS

2. Applicant is
[] a small entity. A statement:
[] is attached.
[] was already filed.
[X] other than a small entity.

EXTENSION OF TERM

NOTE: "Extension of Time in Patent Cases (Supplement Amendments) — If a timely and complete response has been filed after a Non-Final Office Action, an extension of time is not required to permit filing and/or entry of an additional amendment"

CERTIFICATE OF MAILING/TRANSMISSION (37 C.F.R. 1.8(a))

I hereby certify that, on the date shown below, this correspondence is being:

MAILING

- [X] deposited with the United States Postal Service with sufficient postage as first class mail in an envelope addressed to the Commissioner for Patents, P.O. Box 1450, Alexandria, Virginia 22313-14501.

FACSIMILE

- ☐ transmitted by facsimile to the Patent and Trademark Office.

Date:

July 29, 2004

Signature

Peter F. Corless

(type or print name of person certifying)

If a timely response has been filed after a Final Office Action, an extension of time is required to permit filing and/or entry of a Notice of Appeal or filing and/or entry of an additional amendment after expiration of the shortened statutory period unless the timely-filed response placed the application in condition for allowance. Of course, if a Notice of Appeal has been filed within the shortened statutory period, the period has ceased to run." Notice of December 10, 1985 (1061 O.G. 34-35).

NOTE: See 37 C.F.R. 1.645 for extensions of time in interference proceedings, and 37 C.F.R. 1.550(c) for extensions of time in reexamination proceedings.

3. The proceedings herein are for a patent application and the provisions of 37 C.F.R. 1.136 apply.

(complete (a) or (b), as applicable)

(a) ☐ Applicant petitions for an extension of time under 37 C.F.R. 1.136
(fees: 37 C.F.R. 1.17(a)(1)-(4)) for the total number of months checked below:

	Extension (months)	Fee for other than <u>small entity</u>	Fee for <u>small entity</u>
<input type="checkbox"/>	one month	\$110.00	\$55.00
<input type="checkbox"/>	two months	\$420.00	\$210.00
<input type="checkbox"/>	three months	\$950.00	\$475.00
<input type="checkbox"/>	four months	\$1,480.00	\$1,005.00

Fee: \$ _____

If an additional extension of time is required, please consider this a petition therefor.

(check and complete the next item, if applicable)

☐ An extension for _____ months has already been secured. The fee paid therefor of \$ _____ is deducted from the total fee due for the total months of extension now requested.

Extension fee due with this request \$ _____

OR

(b) ☒ Applicant believes that no extension of term is required. However, this conditional petition is being made to provide for the possibility that applicant has inadvertently overlooked the need for a petition for extension of time.

FEE FOR CLAIMS

4. The fee for claims (37 C.F.R. 1.16(b)-(d)) has been calculated as shown below:

(Col. 1) (Col. 2) (Col. 3) SMALL ENTITY					OTHER THAN A SMALL ENTITY			
Claims Remaining After Amendment		Highest No. Previously Paid For	Present Extra	Rate	Addit. Fee	OR	Rate	Addit. Fee
Total	* Minus	**	=	x \$9 = \$			x \$18 = \$	\$ 0
Indep.	* Minus	***	=	x \$43 = \$			x \$86 = \$	\$ 0
[] First Presentation of Multiple Dependent Claim				+ \$145 = \$			+ \$290 = \$	\$ 0
					Total Addit. Fee	OR	Total Addit. Fee	\$

* If the entry in Col. 1 is less than the entry in Col. 2, write "0" in Col. 3,

** If the "Highest No. Previously Paid For" IN THIS SPACE is less than 20, enter "20".

*** If the "Highest No. Previously Paid For" IN THIS SPACE is less than 3, enter "3".

The "Highest No. Previously Paid For" (Total or Indep.) is the highest number found in the appropriate box in Col. 1 of a prior amendment or the number of claims originally filed.

WARNING: "After final rejection or action (§ 1.113) amendments may be made canceling claims or complying with any requirement of form which has been made." 37 C.F.R. 1.116(a) (emphasis added).

(complete (c) or (d), as applicable)

- (c) ☒ No additional fee for claims is required.

OR

- (d) ☐ Total additional fee for claims required \$ _____.

FEE PAYMENT

5. ☐ Attached is a check in the sum of \$ _____.
- ☐ Charge Account No. _____ the sum of \$ _____.
- A duplicate of this transmittal is attached.

FEE DEFICIENCY

NOTE: If there is a fee deficiency and there is no authorization to charge an account, additional fees are necessary to cover the additional time consumed in making up the original deficiency. If the maximum, six-month period has expired before the deficiency is noted and corrected, the application is held abandoned. In those instances where authorization to charge is included, processing delays are encountered in returning the papers to the PTO Finance Branch in order to apply these charges prior to action on the cases. Authorization to charge the deposit account for any fee deficiency should be checked. See the Notice of April 7, 1986, (1065 O.G. 31-33).

6. ☒ If any additional extension and/or fee is required, charge Account No. 04-1105.

AND/OR

☒ If any additional fee for claims is required, charge Account No. 04-1105.



SIGNATURE OF PRACTITIONER

Reg. No. 33,860

Peter F. Corless

(type or print name of practitioner)

Tel. No. (617) 439-4444

EDWARDS & ANGELL, LLP

P.O. Box 55874

P.O. Address

Boston, Massachusetts 02205



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1742

Docket No. 50439-2

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANT: Barstad et al.
SERIAL NO.: 09/605,442 EXAMINER: W. Nicholas
FILED: June 28, 2000 GROUP: 1742
FOR: ELECTROLYTIC COPPER PLATING SOLUTIONS

Mail Stop Amendment
Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

RESPONSE TO OFFICE ACTION

Applicants respond to and request reconsideration of the Office Action dated April 29, 2004 as follows.

Applicants appreciate the notification that all prior rejections have been withdrawn.

Claims 124-132 were newly rejected under 35 U.S.C. 102(e) over newly cited Andricacos et al. (U.S. Patent 6,709,562).

Claims 137-153 were rejected under 35 U.S.C. 102(e) over newly cited Andricacos et al. (U.S. Patent 6,709,562) and further in view of Dahms et al. (U.S. Patent 5,433,840).

At page 3 of the Office Action, the following is stated as grounds for the rejections:

one or more brightener compounds having a molecular weight of about 1000 or less and that are present in a concentration of at least about 1.5 mg per liter (col. 7 "Brightener" with a concentration of 3% by volume. Since 1 mg/L = 0.0001% wt/vol, than 3% vol. ~ 4000 mg/L) of the electroplating composition.

For the sake of brevity, the two rejections are addressed in combination. Such a combined response is considered appropriate because *inter alia* each of the rejections relies on the Andricacos document as the sole or primary citation.

Each of the rejections is traversed.

As discussed at pages 4-5 of the present application, Applicants discovered that use of electroplating baths having high brightener concentrations (1.5 mg/L or greater) are particularly useful for semiconductor copper plating, including to fill microvias and trenches required by current and anticipated semiconductor fabrication requirements.

In this regards, attention is directed to the comparative results detailed at Examples 2 and 3 of the application. In Example 2, using a copper electroplating composition of the invention having a brightener concentration of 2.4 mg/l, semiconductor microvias were filled with copper deposits having no defects as determined by focused beam examination. In comparative Example 3, a copper electroplating composition having a brightener concentration of 0.35 mg/l produced a copper deposit with defects in semiconductor microvias.

The above-noted cited disclosure of the Andricacos patent does not disclose or otherwise suggest Applicants' claimed invention.

More particularly, the cited passage of column 7 of the Andricacos patent reads as follows:

Similar superfilling results are obtained from a solution containing cupric sulfate in the rate from 0.1 to 0.4M, sulfuric acid in the range of 10 to 20% by volume, chloride in the range from 10 to 20% by volume, chloride in the range from 10 to 300 ppm, and LeaRonol additives Copper Gleam 2001 Carrier in the range from 0.1 to 1% by volume, and Copper Gleam 2001 Leveller in the range 0 to 0.1% by volume. Finally, similar superfilling results are obtained from a solution containing cupric sulfate, sulfuric acid, and chloride in the ranges mentioned above and Atotech additives Cupracid Brightener in the range from 0.5 to 3% by volume and Cupracid HS Basic Leveller in the range from 0.01 to 0.5% by volume.

Clearly, that disclosure does not teach or suggest Applicants' invention.

Among other things, the cited disclosure of "Atotech additives Cupracid Brightener in the range from 0.5 to 3% by volume" does not meet Applicants' claim language "one or more brightener compounds that are present in a concentration of at least 1.5 mg per liter of the electroplating composition".

Thus, as is recognized by those working in this area, commercially available additive products are not used as dry, pure chemicals, but instead are used as a formulated composition, particularly as an aqueous formulation. Thus, disclosure of "from 0.5 to 3% by volume" of Cupracid is not a disclosure of any particular amount of brightener concentration, but rather an amount of a formulated product. The skilled worker simply would **not** know the amount of actual brightener that would be employed by such a range of the commercial formulated product; nevertheless, the skilled worker **would** know that the amount of brightener of that range would be much less than the recited range for the commercial formulated product.

This shortcoming in the premise of the instant rejection is apparent in the proposed conversion and amount of brightener set forth at page 3 of the Office Action. Nowhere has any report been cited of brightener concentrations at such levels as proposed at page 3 of the Office Action.

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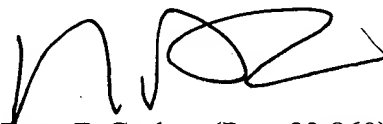
Still further, the composition of the materials reported at the cited column 7 of the Andricacos patent is unknown. See page 5 of the enclosed article "A Review of Copper Plating High Aspect Ratio Plated Through Hole Papers".

Thus, the cited disclosure of the Andricacos patent does not disclose or otherwise suggest use of "one or more brightener compounds having a molecular weight of about 1000 or less" as recited in Applicants' independent claim 124.

In view thereof, reconsideration and withdrawal of the rejections are requested.

It is believed the application is in condition for immediate allowance, which action is earnestly solicited.

Respectfully submitted,

A handwritten signature in black ink, appearing to read 'P. Corless', with a stylized, looping flourish at the end.

Peter F. Corless (Reg. 33,860)
EDWARDS & ANGELL, LLP
P.O. Box 55874
Boston, MA 02205
(617) 439-4444

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A Review Of Copper Plating High Aspect Ratio Plated Through Hole Papers

Contributed by Paul Stransky, CEF, Paul Stransky Associates

23 Aug 1995

Abstract

Eleven papers have been reviewed covering the time period 1986-1991. They represent a mix of highly theoretical to those of a more commercial nature. In general they deal with development of models, application of these models to formulate appropriate plating solutions, and explanations of solution components and their functions.

The purpose of this paper is to try to put the information in a more practical context for platers, who do not have to formulate plating solutions, but have to use them. To help develop an understanding of how copper plating solutions developed for high aspect ratio through holes (HARTH) differ from other plating solutions and what the limitations are if used for multiple plating tasks. For the researcher it summarizes many, but not all of the papers on the subject. However, the references cited in these papers represent significant works on the subject.

REVIEWS

Carano (1) discusses increasing need to plate HARTHS, the effects of throwing power (primary and secondary current distribution), the role of addition agents, solution agitation, other factors such as anode / cathode placement, and ratio, as well as good plating techniques. He concludes process windows will be narrower, and that there has to be a synergism between components of the plating system (chemical, mechanical, electrical).

Amadi (2) discusses primarily plating solution chemistry aspects of HARTH plating. He examines the effects of sulfuric acid, copper concentration, addition agents, and current density on the ratio of surface to hole wall plating thickness. He finds low Copper, high acid, with sulfuric acid:Cu ratio of greater than 20:1, and low current density necessary for maximum uniformity.

Glantz (3) and Hazlow (4) discuss forced flooding and ultrasonics as techniques to insure adequate solution exchange in small holes. This work (3) is primarily about desmear. He uses a model of laminar flow and kinematic viscosity.

Fisher, Sonnenberg and Bernards (5) write about fluid dynamics and electrochemistry. Fundamental aspects of fluid dynamics are discussed using a capillary tube as a model taking contact angle between process solution and substrate into consideration as well

as surface tension. This is followed by a model for looking at mass transfer within a hole during plating, and determining the number of hole volume turnovers needed for a 0.1% depletion rate of copper in the hole not to be exceeded.

Electrochemical factors such as voltage drop within a hole are discussed and a model is developed taking Ohms law and hole geometry into consideration. Experimental work done using a test cell to develop a copper plating solution for HARTHS is described. Results included optimization of metal, sulfuric acid, and organic addition agents. Experimental results were then confirmed with actual drilled boards. In addition general guidelines for equipment, chemistry, and control are also given. Some of the conclusions are:

1. Wetting is not an issue by the time you get to electroplating, because of all the previous preparational steps.
2. Pressure requirements for forced solution flow through holes are minimal and easily met by conventional board agitation.
3. Ohmic potential drop is a very important factor in obtaining uniform plating thickness throughout length of hole. It is the limiting factor determining plating rate.
4. Sulfuric acid/Cu ratio more important than just conductivity re; throwing power (center thickness/surface thickness). Throwing power increases with increasing acid/metal ratio (decreasing metal content).
5. Organic additives (carriers, brighteners, levelers) work to increase the current density or plating rate that can be maintained with satisfactory throwing power.

D'Ambrisi et al (6) approach the subject of small diameter holes (HAR) from the prospect of the entire process. From drilling to electroless plating in this paper. The potential for excessive heat generation and subsequent smear during drilling is discussed.

The importance of adequate desmear, and resulting wettable wall surface is addressed. Different desmear methods (Sulfuric acid, chromic acid, plasma, alkaline permanganate) are covered, with alkaline permanganate recommended.

Several steps of the electroless plating process are explained (conditioning, acceleration, plating). Solution flow with respect to providing appropriate mass transfer of plating solution components (Cu, NaOH, HCHO) is discussed. The model presented is based on laminar flow through a circular cross section and Fick's First Law of Diffusion. The authors conclude that alkaline desmear renders hole walls hydrophilic (wetable), increases surface area by 6x improving adhesion, and aiding small H₂ gas bubble nucleation during electroless plating.

D'Ambrisi et al (7), in a second paper follow up with a discussion of electrolytic and full build electroless copper plating. Problems with ohmic resistance being the limiting factor in uniform HARTH plating are discussed. Full Build electroless copper is suggested as a way around the problem. conclusions include:

1. Mass transport not problem, methods of solution agitation can rectify this.
2. Ohmic resistance is the main problem in achieving uniform plating thickness, with hole length being more important than diameter.
3. Aspect ratios greater than 10:1 can not be plated uniformly.

Yung and Romanki (8) used a gap cell which represented a modified version of a Hull cell equipped for solution flow, and plexiglass drilled boards to study the acid copper PTH process. They were concerned with both plating on the surface and hole wall. Plating solutions with and without additives were used. Mathematical models are developed for electrode kinetics, and mass transfer based on electrochemical engineering principles. Experimental results are correlated with mathematical models.

Three distinct plating regions and mechanisms are described, at extremely low current densities (region I) charge transfer dominates and additives can improve current distribution. At somewhat higher current densities (region II) mixed control prevails, both charge transfer and ohmic resistance, and additives are still effective. In region III at higher current densities ohmic resistance dominates and additives are no longer effective. The authors conclude:

1. Ohmic resistance rather than mass transport is the controlling factor in plating HARTHS at normal current densities.
2. Even with suitable agitation and flow to achieve high mass transfer, high current densities will still give non uniform HARTH wall thicknesses, the model will predict this.
3. Agitation must be balanced on surface and in hole.
4. When ohmic resistance dominates process, its difficult to plate HARTHS above 10:1 without lowering current density to 20-40 mA/cm² (19-38 ASF).
5. Possible schemes to improve copper distribution inside the holes include increasing bath temperature and conductivity, as well as reducing both hole diameter and length.

Hazelbeck (9) develops a nondimensional mathematical model which includes effects of convective, diffusive, and ohmic transport in plating through holes with additives to the bath.

The model which incorporates Laminar flow is used to examine effects of additives and other process variables on deposit uniformity. There are three important dimensionless parameters. The Thiele modulus is a measure of the ratio of reaction rate

to diffusion rate. The inverse dimensionless conductivity measures the ratio of diffusion rate to electrical migration rate. The Peclet number provides a measure of the ratio of convection rate to diffusion rate. Amongst his conclusions are:

1. Uniformity of plating correlated to the three dimensionless parameters.
2. Deposition uniformity can be improved by increasing conductivity when electrodeposition is ohmically controlled.
3. Forced convection in HARTHS is important in improving deposition rate while maintaining uniformity.
4. Additives that decrease cathodic charge transfer coefficient of electrodeposition significantly improve HARTH uniformity.

Hazelbeck, and Talbot (10) review development of thier two dimensional model and other models. The two dimensional model is used to examine the effects of plating variables on through hole thickness uniformity in an acid copper plating bath with and without additives. The general model is used to determine conditions needed to achieve ohmic limited plating necessary for HARTH uniformity. Discussion of various models of plating under limiting conditions such as convective-diffusion, coupled convective-diffusion / ohmic resistance and ohmic resistance are presented. Conclusions include:

1. Uniformity of plating correlated to three dimensionless parameters as described in earlier work above (9).
2. Increased solution conductivity and forced convection in the hole are important in improving deposition rate while maintaining uniformity..
3. A smaller through hole can be plated easier than a larger one of the same aspect ratio.
4. Plating additives that reduce charge transfer can significantly improve HARTH plating uniformity, and with flow enhancement reasonable plating rates of 10-40 mA/cm² (9-38ASF) can be used. Likewise higher plating rates can be achieved for low aspect ratio holes .
5. When using unidirectional flow solution conductivity must be increased or charge transfer reduced by additives.
6. At very high Peclet numbers plating rate is ohmic limited with uniform plating regardless of flow direction.
7. Uniformity of deposition can be improved by increased solution conductivity, use of additives to reduce charge transfer, reducing hole diameter and length while maintaining the same aspect ratio, and lowering current density.

Hazelbeck, and Talbot (11) a model is developed for PTH when two counter electrodes and solution flow reversal is used, and another model for unidirectional flow with only a downstream counter electrode. This work follows from the authors earlier work in(9) and (10) above with the following conclusions.

1. The downstream process allows for higher current densities than with the other configurations while still maintaining plating uniformity. The reason being low metal ion concentration and low ohmic losses at the down stream end of hole with high metal ion concentration and large ohmic losses at the upstream end .
2. Drawback to the downstream process is that it would require holes to be plated separately from surface lines, however it is promising for applications other than PTHs.

DISCUSSION

Some common themes come through from the various investigators:

1. Ohmic resistance within the HARTH is the major limiting factor in obtaining uniform plating.
2. Ohmic resistance is minimized by increasing plating solution conductivity which is accomplished by increasing the ratio of sulfuric acid to copper metal and / or increasing temperature.
3. The use of additives in plating solutions that minimize charge transfer also is very important to hole wall uniformity and the ratio of surface to wall thickness.
4. Plating solution flow is important, with the usual air sparging and panel movement being sufficient to avoid mass transport problems.

Well what does this mean to the plater or plating engineer actually doing the work? We usually do not formulate plating solutions leaving that to our suppliers and at this point in time there are many commercial plating solutions available for HARTH. It may be helpful to understand how commercial plating solutions available for various plating tasks differ from each other.

Table 1 contains a listing of data taken from product literature for 4 different commercial plating solutions (12,13,14,15) designed for different plating tasks. Obviously there is no reference to specific additives since they are proprietary, but for this exercise it is assumed they are appropriate for the task.

The first represents a "standard" copper plating bath for non electronic use (16). Baths 2 and 3 represent the "high throw" acid copper used for many years for PTHs. Bath 4 is representative of baths developed for HARTH plating.

From the table its easy to see the changes that have evolved to increase conductivity, and therefore throwing power (again it is assumed that there have been appropriate additive changes). Copper sulfate, hence copper metal, has been reduced while sulfuric acid has been increased. The ratio of sulfuric acid to copper metal is 1:1 for the "standard", 10:1 for the "high throw", and 38:1 for the "HARTH" baths.

From a practical standpoint there is only one potential problem in attempting to do multiple plating tasks form a single plating

bath. This is probably not true in a large facility where there are dedicated lines. However in a smaller facility there may be. If there are multiple task plating needs amongst which is HARTH, then obviously a more recent HARTH type solution is needed. The problem can arise if a HARTH type bath is also being used for low aspect ratio holes or single sided boards and an attempt is made to use higher than recommended current densities to increase production throughput, this can not be done without burning. From the table again it can be seen that the top end of recommended current density of the HARTH type bath is lower than the others.

The reason for this is with low metal content the plating mechanism becomes mass transport limited at higher current densities, and simply put not enough copper ions can be supplied quickly enough. However in situations like this it might be worthwhile discussing some possible steps to increase mass transport with your particular plating chemistry supplier. These might include increasing solution agitation and temperature. Increasing copper metal temporarily then dummyming it down when HARTH boards have to be run.

The other side of the coin is that a HARTH type plating solution may be a good choice for non electronic applications with complex geometries where throwing power is an issue.

References:

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4. R.E. Hazlow, P.C.Fab, 2, 78, (1989)
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12. Technic TECHNI COPPER-U product data sheet
13. LeaRonal Copper Gleam PCM technical bulletin 30013
14. SelRex CUBATH M product data sheet
15. Shipley Electroposit 1000 product data sheet
16. A.Sato, R.Barauskas, Metal Finishing Guidebook, Hackensack N.J., 1989; p216

Table 1: Comparison Of Properties From Acid Copper Plating Baths

Property	Bath 1	Bath 2.	Bath 3	Bath4
CuSO4 (g/L)	255	75	68	25
Cu (g/L)	57	19	17	6
H2SO4 (g/l)	60	188	173	225
H2SO4:Cu	1:1	10:1	10:1	38:1
Current Density	30-60	1-80	20-40	10-20

Range (A/ft²)

Notes:

1. Techni Copper-U
2. Copper Gleam PCM
3. CUBATH M
4. Electroposit 1000

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